Magnetostriction and ferroelectric state in $AgCrS_2$

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The band structure calculations in the GGA+U approximation show the presence of additional lattice distortions in the magnetically ordered phase of $AgCrS_2$. The magnetostriction leads to formation of the long and short Cr-Cr bonds in the case when respective Cr ions have the same or opposite spin projections. These changes of the Cr lattice are accompanied by distortions of the CrS_6 octahedra, which in its turn leads to development of the spontaneous electric polarization.

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I. INTRODUCTION

Transition metal oxides and sulfides with delafossite structure are actively investigated nowadays due to diverse physical properties observed in these materials. For example, $CuMnO_2$ was found to show a quite strong dependence of magnetic properties on doping [1, 2], $CuAlO_2$ is one of rare $p-$type transparent semiconductors [3, 4], $CuFeO_2$ was intensively studied over past years due to its multiferroicity [5]. Another system with crystal structure closely related to delafossites, $AgCrS_2$, was recently found to be multiferroic [6]. However the mechanism of the coupling between electric and magnetic characteristics in this material is still unknown.

The crystal structure of $AgCrS_2$ is shown in Fig. 1. Triangular planes of Cr ions are stacked along c direction. At very high temperatures it is characterized by the space group $R\bar{3}m$, which is centro-symmetric. With decrease of the temperature to T_c=670 K it transforms to $R3m$, which is still of high symmetry but with lacking inversion and thus noncentro-symmetric. However, spontaneous electric polarization is not observed down to Néel temperature, $T_N \approx 41$ K, where magnetically ordered phase develops [6]. This low temperature phase is characterized by monoclinic noncentro-symmetric Cm space group and doubling of unit cell [7]. Nevertheless the general triangular plane geometry is preserved and it can be regarded as distorted high symmetry. Magnetic structure for $T < T_N$ consists of the double ferromagnetic (FM) stripes coupled antiferromagnetically (see Fig. 4 in Ref. [7]). This magnetic order is developed due to strong antiferromagnetic (AFM) exchange interaction between third nearest neighbors [8].

The absence of the electric polarization in $R3m$ phase is ascribed to disorder of Ag^+ ions [6], that additionally complicates analysis of interplay between electric and magnetic characteristics in $AgCrS_2$. Different scenarios were proposed to get an insight about mechanism of multiferroicity, [7, 9] but this riddle is far from being solved.

In the present paper we performed the optimization of the crystal structure obtained previously in the experiments on powder samples of $AgCrS_2$ and found the presence of additional lattice distortions in the magnetically ordered phase. In the direction perpendicular to the magnetic stripe (in the Cr planes) the chromium ions with the opposite spins become closer to each other and they are moved apart for the same spin projections. These distortions result in the development of spontaneous electric

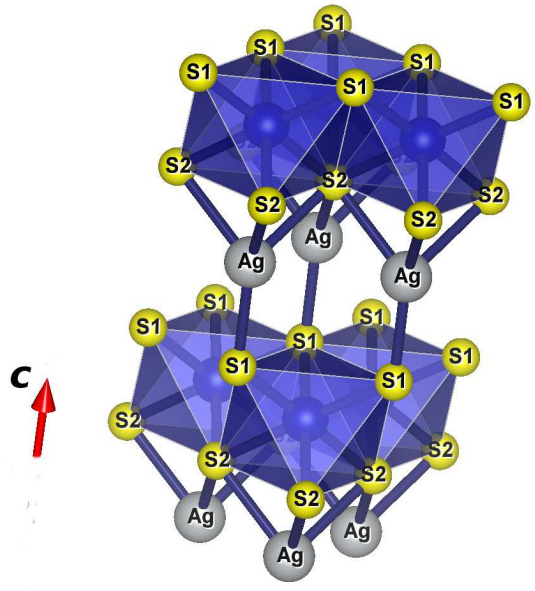

FIG. 1: (color online) Crystal structure of $AgCrS_2$. Cr ions forming triangular planes are shown in blue, while S and Ag ions are in yellow and grey colors, respectively. It is important that there are two crystallographically different sulfur ions: each Ag is connected with one S_1, but with three S_2, which results in different Cr-S bond lengths.

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polarization, which has a magnetostrictive origin therefore.

II. CALCULATION DETAILS

We used pseudo-potential Vienna *ab initio* simulation package (VASP) for the calculation of electronic and magnetic properties of $AgCrS_2$ [10]. The Perdew-Burke-Ernzerhof [11] version of the exchange-correlation potentials was utilized. The strong Coulomb correlations were taken into account via the GGA+U method [12]. The on-cite Coulomb interaction (U) and Hund's rule coupling (J_H) parameters were taken to be U=3.7 eV and J_H=0.8 eV [13, 14]. The integration in the course of the self-consistency was performed over a mesh of 175 **k**-points in the irreducible part of the Brillouin-zone.

The electric polarization was calculated using the Berry phase formalism [15, 16]. The crystal structures of $AgCrS_2$ were taken from Ref. 7. The results presented in Sec. III were obtained for the data corresponding to T=10 K (Cm), while in Sec. IV both T=10 K (Cm) and T=300 K ($R3m$) structures were used.

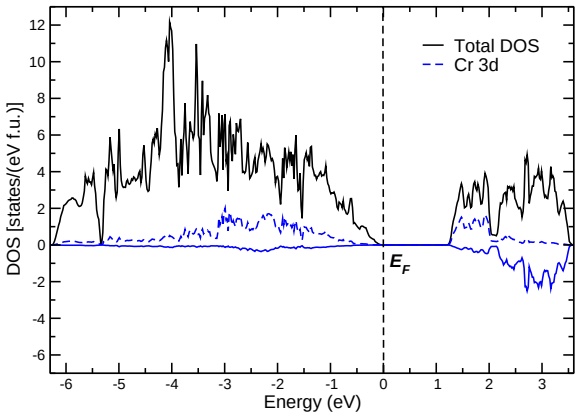

FIG. 2: (color online) Total and partial density of states (DOS) for Cr 3d obtained in the GGA+U calculation for the experimental double stripe magnetic structure. Positive and negative values of partial DOS correspond to spin majority and minority. The Fermi energy is set to zero.

III. ELECTRONIC AND MAGNETIC PROPERTIES AND LATTICE DISTORTIONS

It is interesting to note that oxides based on Cr^{3+} ions are usually Mott insulators [13, 17, 18], where top of the valence band and bottom of the conduction band are formed by the Cr 3d states, and increase of the Cr oxidation state up to 4+ is needed to move them on the verge between Mott and charge-transfer regimes [14, 19–21]. The density of states calculated within GGA+U approximation for experimentally observed magnetic structure are presented in Fig. 2. An analysis of the GGA+U results shows that Cr $3d^{\uparrow}$ states are split and occupied part lies about -4...-2 eV while empty states that form bottom of conduction band are at 1.5...2 eV. The minority spin states, Cr $3d^{\downarrow}$, are totally empty and located at 2...3 eV. Magnetic moment on Cr ions is 2.9 μ_B which is in good accordance with the experimental value of 2.7 μ_B [7]. The top of valence band is formed predominantly by the S 3p states, and thus, $AgCrS_2$ is the charge-transfer insulator. This is related to much larger spatial extension of the S 3p orbitals compared with O 2p. As a result the charge-transfer energy defined as energy costs for the $d^n p^6 \rightarrow d^{n+1} p^5$ transition is drastically decreased in sulfides [22]. The effect of the on-site Coulomb repulsion is also important since it splits partially occupied Cr 3d states and moves them away from the Fermi level. The band gap in $AgCrS_2$ for values of U used was found to be ∼1.2 eV, which is much smaller than in oxides based on the Cr^{3+} ions (e.g. in Cr pyroxenes the band gap is ∼4...5 eV [23]). This can be again attributed to the decrease of charge-transfer energy in sulfides.

In the experimental Cm crystal structure each chromium atom has six in-plane nearest neighbors: two of them lie along b direction on 3.5 Å distance and four Cr are at 3.48 Å distance [7]. The long bonded along b direction Cr-Cr ions form ferromagnetically coupled chain, while these chains are magnetically ordered as ↑↑↓↓ (see Fig. 4 in Ref. [7]). It is important to note that according to experiment the inter-chain distance remains unaltered regardless the ↑↑ or ↑↓ magnetic ordering of different chains. Naively thinking one may expect that magnetostriction differentiates the distances between FM (↑↑) and AFM (↑↓) coupled chains and therefore the crystal structure could be somewhat different from the one reported previously.

In order to clarify the discrepancy between experiment and theoretical considerations we carried out the structural optimization of the low temperature phase using GGA+U method. The total energy calculations for experimental parameters display that double stripe AFM order does not correspond to the ground state, being 1.7 meV/f.u. higher than FM state. The relaxation of the atomic positions and lattice parameters dramatically changes this situation stabilizing the double stripe magnetic structure and making this magnetic order the lowest in total energy.

An analysis of the relaxed atomic positions for the double stripe AFM structure shows that the Cr-Cr distance along stripe stays the same, $d_{||}$=3.5 Å, while in perpendicular directions they change substantially: Cr-Cr bonds with the same spin projection are stretched, $d_{\perp}^{\uparrow\uparrow} = d_{\downarrow\downarrow}$=3.52 Å, and with opposite spins are shrunk, $d_{\perp}^{\uparrow\downarrow}$=3.44 Å (see Fig. 3). However the relaxation does not lead to corrugation of the Cr planes leaving average Cr-Cr distance the same (3.48 Å) in the directions perpendic-

ular to the stripe. Thus the effect of the magnetostriction for Cr-Cr bond lengths exceeds $\delta d_\perp = d_\perp^{\uparrow\uparrow} - d_\perp^{\uparrow\downarrow} \sim 0.04$ Å for given U. For the FM order relaxation leads to the minor changes of the crystal structure.

It has to be noted that the effect of magnetostriction depends strongly on the value of the on-site Coulomb repulsion parameter U. For example, the decrease of U on 1 eV results in increase of $\delta d_\perp$ (up to 0.05 Å). One of the possible explanations could be that we gain magnetic energy moving some of the Cr nearest neighbors closer together. For short Cr-Cr pairs corresponding exchange interaction has to be AFM, since the direct exchange should dominate over other contributions in the edge sharing geometry [8]. This is exactly observed in the present calculations: Cr ions having opposite spin projections are getting closer. Moreover, a decrease of the Coulomb interaction parameter increases this effect since direct exchange is inverse proportional to it, $\sim 1/U$. The gain in magnetic energy due to direct exchange in $\uparrow\downarrow$ pairs is compensated by the growth of the elastic energy and decrease of the magnetic energy gain in $\uparrow\uparrow$ ($\downarrow\downarrow$) Cr pairs, so that an exact value of $\delta d_\perp$ depends on details on different internal parameters of the system.

It was found in Ref. [8] that in the LSDA (local spin density approximation) the double stripe AFM structure in $AgCrS_2$ is stabilized due to strong AFM exchange coupling between the third nearest neighbours. While the magnetostriction, as it was explained above, will certainly modify nearest neighbour interaction the exchange to the third nearest neighbours will not be changed drastically because of unaltered average distances in chromium plane.

IV. ELECTRIC POLARIZATION

For the calculation of the electric polarization (P) one needs to choose a reference structure and find the difference (δP) in polarizations for given and reference structures [24]. One usually takes the high temperature centro-symmetric lattice as the reference. However, as it was explained above in $AgCrS_2$ the polarization appears at the transition between two noncentro-symmetric structures, $R3m$ and Cm. Therefore in spite of the fact that real reason of the absence of electric polarization in intermediate temperature $R3m$ structure is unknown [6], we are forced to consider this structure as the reference.

The transition from paraelectric to ferroelectric state is accompanied by the transition from paramagnet to AFM with formation of the long-range magnetic order. The paramagnetic state having local spins and short-range magnetic correlations can hardly be simulated in the GGA or GGA+U calculations. In principle one may model this state with such a technique as averaging over different spin configurations [25], but even in this case this state is useless since for Cr^{3+} with $3d^2$ electronic configuration LSDA/GGA is expected to give a metal and hence one cannot calculate P. The nonmagnetic state

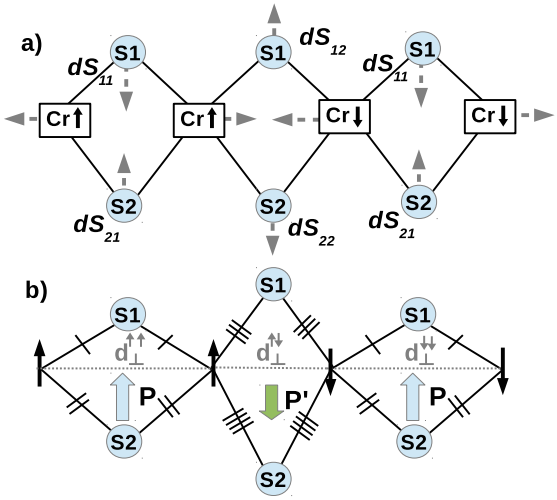

FIG. 3: (color online) a) Distortions dS_{11}, dS_{12}, dS_{21}, dS_{22} (grey dashed arrows) which appear in experimentally observed double stripe AFM order due to magnetostriction. The direction perpendicular to double stipes ($\uparrow\uparrow\downarrow\downarrow$) is shown. Black arrows show the spin order. $dS_{11} \neq dS_{12} \neq dS_{22} \neq dS_{22}$. b) Distorted structure and corresponding electric polarization. Note that since the distortions in two neighboring CrS_6 octahedra are different, $\vec{P}$ and $\vec{P}'$ do not compensate each other.

could neither be used, since the electronic configuration of each Cr^{3+} ion would be not $(d\uparrow)^3$, but $(d\uparrow)^{1.5}(d\downarrow)^{1.5}$, which is quite unnatural because of the absence of the local spin. The isotropic AFM state (all Cr neighbours are antiferromagnetically coupled) which would be the best to simulate paramagnet is also impossible due to frustrated triangular lattice. Therefore we simulate reference paraelectric state by the $R3m$ crystal structure with the FM order.

On the first stage we calculate δP due to appearance of the double stripe AFM order in the $R3m$ structure, relaxing atomic positions both for the double stripe (2S) AFM and FM orders. This results in $|\delta\vec{P}_{2S\to FM}| \sim 2600\mu C/m^2$ and polarization was found to be directed perpendicular to the Cr triangular planes (i.e. along rhombohedral c axis). We also checked that the use of the antiferromagnetically coupled AFM ($\uparrow\downarrow\uparrow\downarrow$) chains as the reference state does not change the result.

Since for the $R3m$ structure the lattice parameters are known only for quite high temperature (300 K, much above transition to ferroelectric state) and the unit cell volumes V_{R3m}^{300K} and V_{Cm}^{10K} are different, we repeated these calculations for the value corresponding to the lowest in temperature structure and found that $|\delta\vec{P}_{2S\to FM}| \sim 2800\mu C/m^2$, i.e. practically does not change. Moreover, additional calculation for the $R3m$ structure, but with fixed ionic positions (i.e. there is only electronic contribution to the polarization) gives $|\delta\vec{P}^{elec}_{2S\to FM}| \sim 1900\mu C/m^2$. I.e. it is a redistribution of the electronic charge density due to the double stripe AFM structure that mainly leads

to the development of the spontaneous electric polarization in the low temperature phase of $AgCrS_2$. The lattice follows this tendency and changes the absolute value of the polarization.

The double stripe magnetic structure was shown to induce ferroelectric state due to specific lattice distortions in CdV_2O_4 [26], which seems to be related with the orbital-selective behavior [27, 28]. While the crystal structure is quite different in case of $AgCrS_2$ (delafossite-like instead of spinel), the microscopic mechanism beyond the ferroelectric state is similar.

In the $R3m$ crystal structure there are two inequivalent sulfur atoms (S_1 and S_2 in Fig. 1) with different chromium-sulfur bond lengths [7]. In effect already in the experimental $R3m$ structure the Cr-S_1-Cr and Cr-S_2-Cr triangles (formed by two neighboring Cr and one of the common S) are also different in terms of angles and bond lengths Cr-S, as shown in Fig. 3. The magnetostriction results in the formation of short ($d_\perp^{\uparrow\downarrow}$) and long ($d_\perp^{\uparrow\uparrow}$) metal-metal bonds (see Fig. 3). As a result two neighboring Cr↑-S_1-Cr↑ and Cr↑-S_1-Cr↓ triangles turn out to be differently distorted (the same is valid for two adjacent triangles with S_2 ions). These $dS_{11}, dS_{12}, dS_{21}, dS_{22}$ distortions do not compensate each other, which leads to non-zero electric polarization. It has to be noted, that while this mechanism is based on specific atomic displacements, the distortions by themselves are triggered by different charge-density distributions for the ↑↑ (↓↓) and ↑↓ bonds.

Albeit the magnetostriction strongly modifies all bond lengths, both Cr-S_1-Cr and Cr-S_2-Cr triangles stay isosceles, as shown in Fig. 3b. Therefore there is no component of the electric polarization along Cr-Cr bonds. In contrast since all the displacements, dS_{ij}, are different in two neighboring plaquettes (Cr↑-S_1-Cr↑-S_2 and Cr↑-S_1-Cr↓-S_2), there are two resulting polarizations $\vec{P}$ and $\vec{P}'$, which lie in the planes of plaquettes, perpendicular to Cr-Cr bonds. Each CrS_6 octahedron from the double chain (AFM double chain) share its edges with two neighboring octahedra and the net polarization is directed nearly perpendicular to the CrS_2 plane as shown in Fig. 4.

V. CONCLUSIONS

The total energy calculations in the GGA+U approximation for the low temperature Cm crystal structure of $AgCrS_2$ compound show an importance of atomic relaxation to set the experimentally observed magnetic order as ground state. The relaxed atomic positions for Cr ions display the changes of distances between FM chains that coupled ferro- and antiferromagnetically. Therefore on the base of the first principles calculations we predict the existence of magnetostriction effect in this material which was not observed in experiment [7]. The evaluated electric polarization is mostly due to electronic rather structural origin and it is much larger than 20 $\mu C/m^2$ measured experimentally [6]. This discrepancy can be partially explained by the improper ferromagnetic (not paramagnetic) reference point (which we are forced to use) to calculate initial polarization. The calculations that treat properly the insulating nature of material at all temperatures and paramagnetism with local moments at high temperatures and long range magnetic order at low temperatures can be done within DFT+DMFT method. In this case one would expect that the calculated value of electric polarization will be reduced. At the same time the experimental estimation of the electric polarization was obtained on the polycrystalline samples [6], which are known to provide substantially smaller values than in single crystals, due to features of the pyroelectric measurements, see e.g. Refs. [29–32]. The use of polycrystalline samples could also explain the absence of the magnetostriction effect in experiment. Therefore, the DFT+DMFT calculations as well as refined measurements on single crystal samples are required for further investigation of the electronic and magnetic properties of $AgCrS_2$.

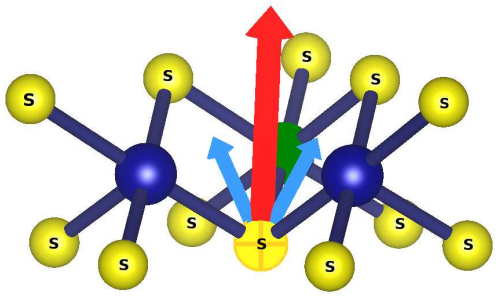

FIG. 4: (color online) Two net electric dipole moments (shown in blue) in two Cr_2S_2 plaquettes form net polarization (shown in red) which is directed nearly perpendicular to the CrS_2 plane. The plaquettes do not lie in the same plane (in contrast to Fig. 3). Blue and green balls correspond to Cr ions with different spin projections.

VI. ACKNOWLEDGMENTS

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